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Example of Disulfide Conformational Change in the Solid State: Preparation, Optical Properties, and X-ray Studies of a Cystamine-Based Iodoplombate Hybrid

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A novel cystamine-based hybrid, namely, α-[{$NH_3(CH_2)_2SS$-$(CH_2)_2NH_3$}PbI_6]·$2H_3O$ (**1a**), was prepared under solvothermal conditions. Interestingly, **1a**, which is built up from isolated PbI_6 octahedra, can be easily changed into its polymorph, namely, β-[{$NH_3(CH_2)_2S$–$S(CH_2)_2NH_3$}PbI_6]·$2H_3O$ (**1b**) only by heating it up to 45 °C. According to the results of X-ray diffraction analyses, the polymorphic phenomenon of **1a** and **1b** results from a conformational change in the helical diprotonated cystamine cation in the solid state. Both **1a** and **1b** crystallized in the orthorhombic *Pna*2_1 space group. The reversibility of this transformation is proved by single-crystal X-ray diffraction and second harmonic generation measurements.

Introduction

As is well known, disulfides (R–SS–R′) are inclined to form screwed structures in solution as well as in crystalline states, as both enantiomeric conformations display chiral *P*- and *M*-helical forms.[1] The disulfide functionality is an important feature of proteins and biologically active polypeptides due to its ability to form complexes (especially in the case of polyfunctional disulfide ligands) and its inherent chirality, which may transmit stereochemical information, as suggested for instance in Prion proteins.[2] In material science, organic disulfides can be used as moderate donors towards soft metal ions, as well as flexible ligands in the field of coordination polymers.[3] In the course of our investigations on perovskite-like compounds, we recently focused on the synthesis of halogenometalates of Bi^{III} and Pb^{II} hybrid materials containing the diprotonated cystamine molecule $[H_3N(CH_2)_2S–S(CH_2)_2NH_3]^{2+}$, here denoted by *H₂cys*.[4–6] Although the conformational change in disulfides (leading to racemization) is well known in solution due to the relatively low barrier of rotation of S–S bonds (in the case of nonbulky R- and R′- organic groups),[7] we recently showed that the disulfide-based cystamine molecule was also able to change its conformation in the solid state. Thus, the α-[(H_2cys)PbI_5·H_3O] phase was transformed into the β-[(H_2cys)PbI_5·H_3O] phase as a result of a conformational change in the half molecules. This phenomenon was described as an exceptional conglomerate to true racemate reversible transition in the solid state.[4] More recently, a similar phenomenon, that is, a helical conformational change, was also observed in the parent bismuth compound leading to polymorphs α- and β-(H_2cys)BiI_5.[5] In both cases, hybrids, which are based on MI_5 chains of corner-shared MI_6 octahedra, undergo a reversible acentric-to-centric structural transition, making them good candidates for SHG switches controlled by temperature. In the broad field of nonlinear optic (NLO) materials, the incorporation of switchability into the NLO behavior is of high interest for applications in optoelectronic or photonic technologies.[8] Herein, we report on the preparation, X-ray structural characterization, and NLO properties of a new cystamine-based hybrid, α-[(H_2cys)PbI_6·$2H_3O$] (**1a**), that undergoes solid-state helical conformational change to give polymorph β-[(H_2cys)PbI_6·$2H_3O$] (**1b**) at 45 °C. The reversibility of this single-crystal-to-single-crystal process is proved by results of single-crystal X-ray diffraction and second harmonic generation (SHG) measurements. Although both structures are acentric, the intensity of the SHG signal of **1a** is much higher than that of **1b**.

Results and Discussion

The crystals of α-[(H_2cys)PbI_6]·$2H_3O$ (**1a**) were prepared under solvothermal conditions at 100 °C from an equimolar mixture of PbI_2 and $H_2NCH_2CH_2S$–$SCH_2CH_2NH_2$·2HCl dissolved in acetonitrile solution containing an amount of concentrated hydriodic acid. It must be noted that lower

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temperatures lead to crystals of [(H_2cys)PbI_5]·H_3O,[5] whereas longer experiment times at 100 °C favor the decomposition of cystamine as well as the formation of NH_4I. The phase transition between **1a** and **1b** does not affect the crystalline quality, which allows us to perform a complete X-ray diffraction study by using one single crystal (data collected at 293 K and 323 K for **1a** and **1b**, respectively).

Both structures are built up from isolated $Pb^{II}I_6$ octahedra, cystamine, and hydronium cations. The structure of the high-temperature phase (**1b**) can be considered as a substructure of **1a**, as its a axis (a_β) corresponds to $a_\alpha/3$. All cystamine cations are disordered over two positions in **1b**, and both components, whose occupation rates are 0.37 and 0.63, respectively, adopt the same helical form (Figure 1b). Nevertheless, because of glide plane symmetries, both *M*- and *P*-helical forms are incorporated in the structure of **1b** (Figure 2b, disordered atoms are omitted for clarity). On the contrary, both components of the two disordered molecules in **1a** have opposite chirality (Figure 1a), and the occupation factors of main molecular components are 0.66 (S1–S2 disulfide-based molecule) and 0.59 (S3–S4 disulfide-based molecule). Other structural features characterize each phase. Thus, one iodide belonging to one of the three independent PbI_6 polyhedra is disordered over two positions in **1a**, whereas all lead polyhedra possess a disordered iodide in **1b** (Figure 2). By plotting main components of disordered molecules on one hand, and three consecutive cells of the structure of **1b** on the other hand (Figure 2a), it is easy to compare both structures and to understand the helical conformational change in cystamine during the transition, as already observed in other halogenometalate salts.[5,6] For instance, all molecules in the (a,c) plane of **1b** possess the same chirality, *M* or *P*, whereas both *M* and *P* conformations are observed in the (a,c) plane of **1a**. The ability of cystamine entities to change their conformation in the solid state is an interesting feature, but it can appear quite surprising considering the required energy cost and the required space. It is worth noting that the transition is athermic, which means that it is driven by the expected increase in entropy of the system. Anyway, as already under-

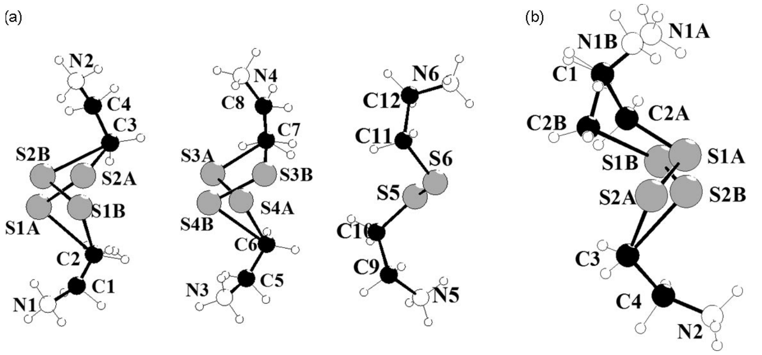

Figure 1. The conformations of the cystamine cations in **1a** and **1b**. Some atoms are disordered over two positions, leading to A (major) and B (minor) components [torsion angles: **1a**: C2–S1A–S2A–C3 94.2(10)°, C2–S1B–S2B–C3 –94.1(13)°, C6–S4A–S3A–C7 84.7(9)°, C6–S4B–S3B–C7 –99.3(11)°, C10–S5–S6–C11 –85.7(10)°; **1b**: C3–S2A–S1A–C2A –87.0(15)°, C3–S2B–S1B–C2B –78.2(15)°].

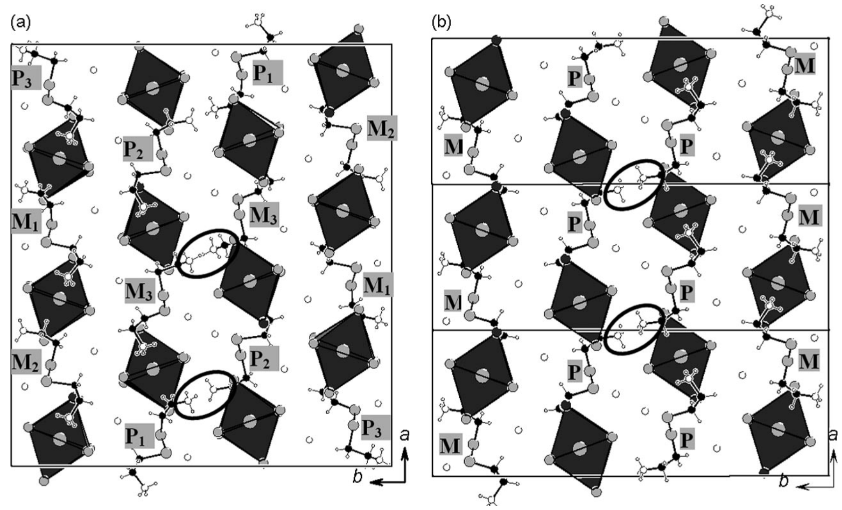

Figure 2. Structures of **1a** (one unit cell, a) and **1b** (3 unit cells, b) viewed along the c axis. For clarity, only the major components of the disordered atoms are plotted. *P* and *M* indicate the different kinds of chiral helicity. Numerical suffixes are added for the different independent molecules (1, 2, and 3 for S1–S2, S3–S4, and S5–S6 disulfides, respectively). Disordered iodides are drawn as dark-grey spheres. Selected pairs of ammonium groups are marked in circles.

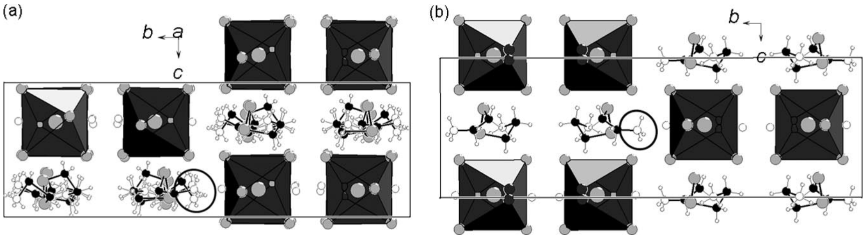

Figure 3. Structures of **1a** (left) and **1b** (right) viewed along the *a* axis. For clarity, only the major components of the disordered molecules are plotted. Disordered iodides are drawn as dark-grey spheres. Selected ammonium groups are marked in circles.

lined in the case of the more simple structure of [(H_2cys)-PbI_5]·H_3O, we can speculate that hydrogen bonding at the organic–inorganic interface, and more precisely a change in it, seems to play a major role in helical conformational changes. First, let us observe that the ammonium heads make intramolecular interactions with the disulfides through hydrogen bonds, which by the way involve the helical form of the whole molecule (see Figure 1). A change in the hydrogen bonding at the organic–inorganic interface, that is, a change in the position of the ammonium heads (see marked nondisordered NH_3 groups in Figures 2 and 3), probably destabilizes the disulfide bridges, resulting in helical conformational change.

Both structures crystallized in the acentric space group *Pna*2_1. Pseudosymmetry of the mirror perpendicular to *c* can be found in the structure, especially when only the positions of the heavy atoms are considered. However, this hypothesis is false after accurately investigating the positions of all atoms (Figure 3). This is also unambiguously proved by the results of SHG measurements, as the SHG properties are only available in acentric structures. The SHG measurements are performed by applying the Kurtz and Perry model[9] (1064 nm beam of a Nd:YAG pulsed laser). The effective second-order nonlinear susceptibility of **1a** (0.3 $pm V^{-1}$) is about 2.5% of POM (3-methyl-4-nitropyridine-1-oxide, used as reference).[10] The intensity of the SHG signal as a function of temperature shows a monotonous behavior up to 53 °C followed by an abrupt decrease to approximately one tenth of the initial value (Figure 4, heating rate of 0.3 $°C min^{-1}$). This result is in good accordance with the acentric structure of the high-temperature phase, whereas it is different from the behaviors of [(H_2cys)-PbI_5]·H_3O[4] and (H_2cys)BiI_5[5] in which the SHG intensities go down to zero at high temperature, because their phase transformations are between acentric and centric structures. When the sample is cooled down at a rate of 0.3 $°C min^{-1}$ to 35 °C, the intensity of the SHG signal increases, first rapidly and then slowly, to reach the initial value at room temperature. As shown in Figure 4, there is an obvious hysteresis in the curve of the SHG intensity to the temperature, which indicates that such compounds can be considered as good candidates for an SHG switch controlled by temperature or optically sensitive detector of temperature.

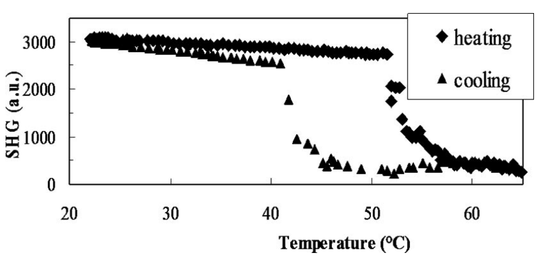

Figure 4. The change in the SHG intensity in the crystallized powder sample of **1a** as a function of temperature.

Conclusions

An organic–inorganic hybrid based on cystamine, hydronium, and isolated PbI_6 octahedra was synthesized. This hybrid, namely, α-[(H_2cys)PbI_6·$2H_3O$] (**1a**), undergoes a reversible structural transition under moderate conditions (T = 45 °C) leading to the β-[(H_2cys)PbI_6·$2H_3O$] (**1b**) phase, whose structure is a substructure of **1a** ($a_\beta = a_\alpha/3$). In the structures, the cystamine molecules are disordered over two positions, and both components have opposite chiralities in **1a**, whereas they are the same in **1b**. The conformational change in the disulfide molecules in the solid state through the transition results in an abrupt decrease in the SHG intensity, thus revealing that **1a** can be considered as a candidate for an SHG switch that can be controlled by temperature. This interesting phenomenon of conformational change in the solid state seems to be mainly related to a change in weak interactions, including hydrogen bonding, at the organic–inorganic interface. Although such a transformation was first observed in parent compounds based on flexible MI_5 (M = Pb, Bi) chains that can display different conformations, we show that it can occur in cluster-based structures. In order to achieve switchable NLO materials controlled by different stimuli, we will further consider the use of photochromic entities as polyoxometalate clusters in our system, because the metal photoreduction process was proved to be associated with a change in hydrogen bonding at the organic–inorganic interface.[11]

Experimental Section

[(H_2cys)PbI_6]·$2H_3O$ (1a): This compound was prepared under solvothermal conditions. Hydriodic acid (2 mL, *Fw* = 80.92, *d* = 1.49, 48%) was added to an acetonitrile solution (6 mL) of PbI_2 (126.12 mg, 0.273 mmol) and $H_2NCH_2CH_2S–SCH_2CH_2NH_2·2HCl$

(118.02 mg, 0.524 mmol). The solution was sealed in a 25-mL Teflon-lined PARR autoclave and heated up to 100 °C within 6 h. The temperature was kept at 100 °C for 24 h and then cooled to room temperature within 30 h. Yellow block crystals of **1a** together with transparent crystals of NH_4I were obtained. The crystals were then filtered and washed with cold ethyl acetate and dried at 40 °C. Crystals of **1a**, which were separated by hand under a binocular microscope, are quite hygroscopic and must be kept under a dry atmosphere. All of the reflections in the XRPD pattern can be indexed in the orthorhombic cell of **1a**.

Thermal Analysis: Differential scanning calorimetry (DSC) and thermogravimetric (TGA) measurements were performed with DSC-2010 and TGA2050 TA Instruments systems, in the temperature range 20–350 °C and 20–900 °C, respectively (see the Supporting Information). Surprisingly, there is no peak in the DSC curve around the temperature of transition as detected both by SHG and X-ray diffraction measurements. Compound **1b** is stable up to 200 °C and then decomposes in two steps up to 600 °C.

X-ray Crystallography: X-ray diffraction data of a selected single crystal were collected with a Bruker-Nonius KAPPA-CDD diffractometer equipped with a graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å). A summary of crystallographic data and refinement results for both polymorphs is listed in Table 1. Structures were solved and refined by using the SHELXL97 package. Heavy atoms (Pb, I, S) were first located by using direct methods, and the C and N atoms were then located from the analysis of the Fourier difference maps. Positions and agitation parameters were refined by full-matrix least-squares routines against F^2. All hydrogen atoms were treated with a riding model. In **1a**, there are three independent cystamine cations in the lattice, and two of them are disordered. For both cations, sulfur atoms were located on two positions, leading to S1A–S2A or S1B–S2B and S3A–S4A or S3B–S4B disulfides. The refined occupation factors of atoms belonging to a same pair (e.g. S1A/S2A) were constrained to be equal as were the agitation parameters of disordered atoms (e.g. S1A/S1B). Finally, occupations factors were refined to 0.59 (S1A/S2A), 0.41 (S1B/S2B), and 0.66 (S3A/S4A), 0.34 (S3B/S4B) for the two molecules, respectively. Some C atoms display quite high isotropic agitation parameters [in the $(0.105–0.195)\times10^{-3}$ Å^2 range], then several bond lengths are over expected ranges, especially the bonds in the minor component (S1B, S2B, ...). In this situation, the statistical disorder is too complicated to be treated properly. However, in the major component, the cations, bond lengths, angles, and torsion angles of the CSSC cores are quite acceptable, and the chirality of the molecules was unambiguously defined. A statistical disorder also affects one iodide belonging to one of the three independent PbI_6 octahedra. Finally, refinements of positions of all non-H atoms and of anisotropic displacement parameters of Pb, I, O, and S5, S6 atoms result in R = 0.045. In **1b**, the asymmetric unit contains one PbI_6 entity and one disordered molecule. One iodide atom is disordered over two positions as well as one N atom and a –CSS– fragment of the cystamine entity. The refined occupation factor of atoms belonging to the same molecular component (e.g. N1A/C2A/S1A/S2A) was constrained to be equal as well as the agitation parameters of disordered atoms (e.g. S1A/S1B). Finally, occupations factors were refined to 0.63 (A component) and 0.37 (B component). The bond lengths and angles in the major components are close to the expected values. On the contrary, some bond lengths and angles in the minor components are quite far from the expected ones, which probably reveal an incompletely treated disorder that could not be further improved in this situation. Refinements of positions of all non-H atoms and of anisotropic displacement parameters of Pb, I, and O atoms lead to R = 0.042.

Table 1. Crystallographic data for **1a**, **1b**.

	α-[(*SS*)$PbI_6\cdot2H_3O$] (**1a**)	β-[(*SS*)$PbI_6\cdot2H_3O$] (**1b**)
Fw [g mol^{-1}]	1160.93	1160.93
Space group	orthorhombic $Pna2_1$	orthorhombic $Pna2_1$
a [Å]	30.166(9)	10.0340(6)
b [Å]	27.418(3)	27.473(2)
c [Å]	8.9962(12)	9.0118(11)
V [Å^3]	7441(1)	2484.2(4)
Z	12	4
Observed reflections [$I > 2\sigma(I)$]	8223	5158
Parameters	376	140
R_1 [$I > 2\sigma(I)$]	0.045	0.042
wR_2 (all data)	0.084	0.111

CCDC-691809 and 691810 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/datarequest/cif.

NLO Measurements: The polycrystals of **1a** and POM were grinded and sieved in order to control the grain size (range of 125–250 μm). The powder samples were crushed tightly between two microscope slides to form slices, and the slides were installed in the beam of laser. All experiments were carried out under the same conditions, especially the amounts of different samples. The SHG measurements were performed by applying the Kurtz and Perry method[9] with powder samples (fundamental excitation wavelength at 1064 nm). The power of the fundamental beam was tuned with a halfwave plate and a Glan polarizer. The beam was focused on the sample by a convergent lens with a focus of 250 mm. The SHG signals were detected by a photomultiplier tube (Hamamatsu R1828-01), then integrated by a boxcar integrator, and processed by a computer. Heating and cooling speeds of 0.3 °C min^{-1} were used for temperature-dependent SHG experiments.

Supporting Information (see footnote on the first page of this article): Additional structure refinement details of **1a**,**b**; single-crystal X-ray diffraction images; powder X-ray pattern; thermal analysis (TGA, DSC); experimental setup of the SHG experiment.

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